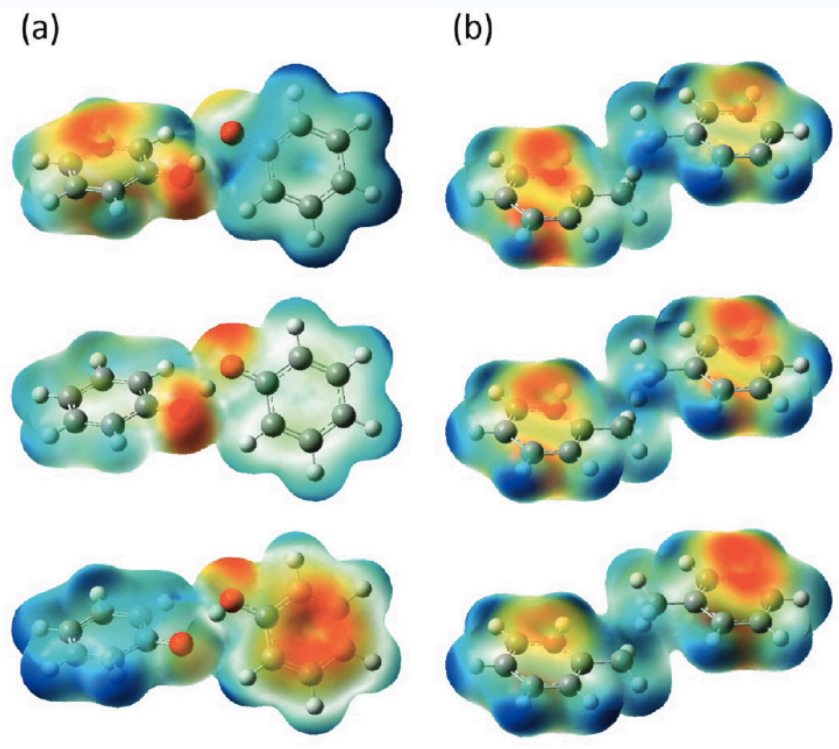


# Wave function approaches to non-adiabatic systems

Norm Tubman

# Breakdown of Born-Oppenheimer

- There are many physical systems that require theory beyond the Born Oppenheimer approximation in order to be treated accurately.

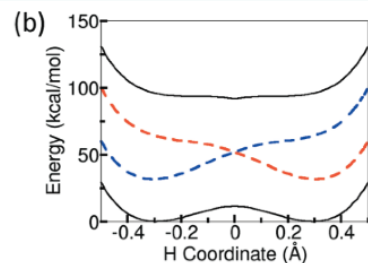
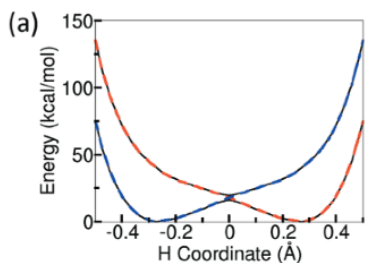
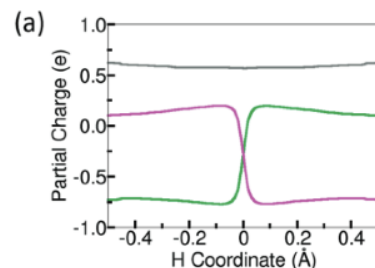
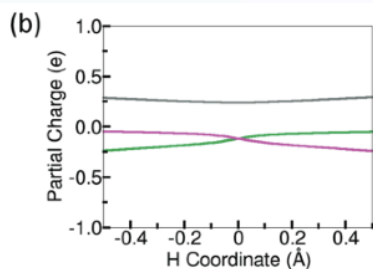


Phenoxy-phenol

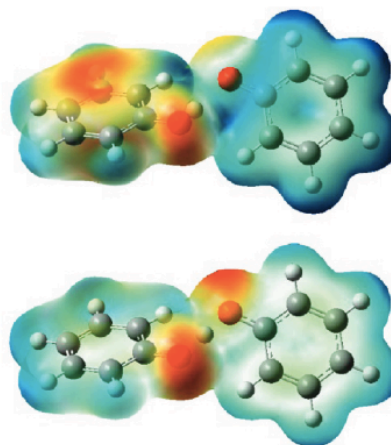
toluene

From Sirjoosingh et. al. JPCA

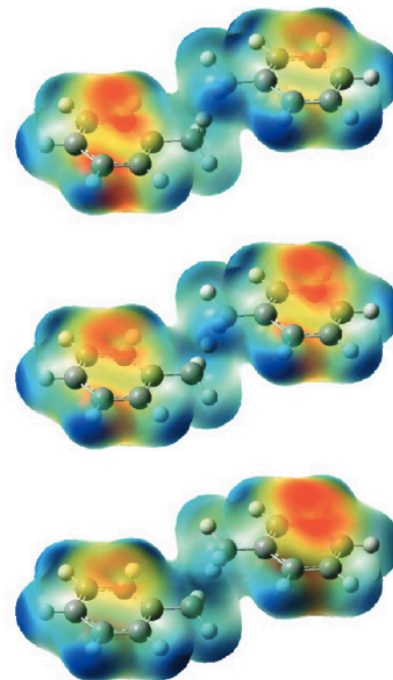
# Breakdown of Born-Oppenheimer



(a)



(b)



Phenoxy-phenol

toluene

From Sirjoosingh et. al. JPCA

# Born Oppenheimer Approximation

- The full Hamiltonian should have kinetic energy for both the electrons and the ions
- The clamped nuclei Hamiltonian is obtained by setting the nuclear kinetic energy equal to zero.
- The full wave function can be expanded in terms of the solution of the clamped nuclei Hamiltonian and nuclear functions that are can be considered expansion coefficients

$$\hat{H}(\mathbf{R}, \mathbf{r}) = \hat{T}_n(\mathbf{R}) + \hat{T}_e(\mathbf{r}) + \hat{U}(\mathbf{R}, \mathbf{r})$$

$$\hat{H}_{cl}\Phi_i(\mathbf{r};\mathbf{R}) = V_i(\mathbf{R})\Phi_i(\mathbf{r};\mathbf{R}).$$

$$\Psi(\mathbf{R}, \mathbf{r}) = \sum_i \chi_i(\mathbf{R})\Phi_i(\mathbf{r};\mathbf{R}),$$

This expansion is expected to be exact, although it has never been proven

# Born Oppenheimer Approximation

- The full Hamiltonian can be expanded in this basis set. The Lambda terms are the non-adiabatic coupling operators
- The Born Oppenheimer approximation is obtained by reducing the wave function ansatz from a sum over states to just one state. This definition is not unique!
- The adiabatic approximation is obtained by setting the non-adiabatic coupling operators equal to 0

$$[\hat{T}_n + V_j] \chi_j - \sum_i \hat{\Lambda}_{ji} \chi_i = i\hbar \frac{\partial \chi_j}{\partial t}$$

$$\hat{\Lambda}_{ji} = \delta_{ji} \hat{T}_n - \langle \Phi_j | \hat{T}_n | \Phi_i \rangle$$

$$\Psi(\mathbf{R}, \mathbf{r}) = \chi(\mathbf{R}) \Phi(\mathbf{r}; \mathbf{R}).$$

$$[\hat{T}_n + V - \hat{\Lambda}] \chi = i\hbar \frac{\partial \chi}{\partial t},$$

# The adiabatic approximation

$$[\hat{T}_n + V] \chi = \epsilon \chi,$$

- Binding curves for the  $C_2$  molecule. This is calculated by solving the electronic Hamiltonian at different ionic coordinates
- Different potential energy surfaces arise from the excited states

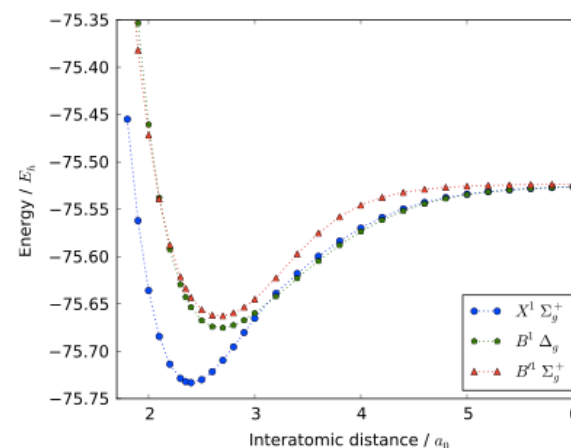
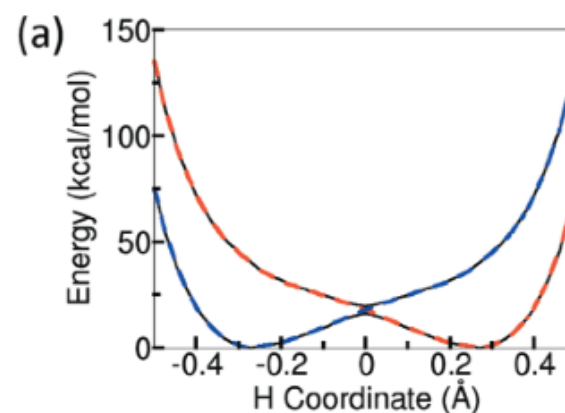


Fig. 4. Bond dissociation curves for the low-lying  $1A_g$  states of the carbon dimer in the cc-pVDZ basis.



# Born Oppenheimer Approximation

- We can try to solve the full Hamiltonian with no approximations, but it is very difficult

$$[\hat{T}_n + V_j] \chi_j - \sum_i \hat{\Lambda}_{ji} \chi_i = i\hbar \frac{\partial \chi_j}{\partial t},$$

- We can rewrite Lambda in terms of energy differences between the separate potential energy surfaces
- When the difference in energy between states becomes small, then Lambda diverges, and it does not make sense to use the Born Oppenheimer approximation

$$\hat{\Lambda}_{ij} = \frac{1}{2M} (2\mathbf{F}_{ij} \cdot \nabla + G_{ij})$$

$$\begin{aligned} \mathbf{F}_{ij} &= \langle \Phi_i | \nabla \Phi_j \rangle \\ &= \frac{\langle \Phi_i | (\nabla \hat{H}_{\text{el}}) | \Phi_j \rangle}{V_j - V_i} \end{aligned}$$



# Approaches to going beyond Born Oppenheimer

- **Nuclear Electron Orbital Methods** (HF, CASSCF, XCHF, CI)

Basis set techniques that make explicit use of the Born Oppenheimer approximation to generate efficient basis sets for wave function generation

- **Correlated Basis** (Hylleraas, Hyperspherical, ECG)

Generic basis set technique that uses explicitly correlated basis sets to solve the electron-ion Hamiltonian to high accuracy.

- **Path Integral Monte Carlo**

Finite temperature Monte Carlo technique based on thermal density matrices

- **Fixed-Node diffusion Monte Carlo**

Ground state method that is based on generating high quality wave functions and projecting to the ground state wave function

- **Multi-component density functional theory**

Density functional theory for electrons and ions simultaneously



# Outside perspective on QMC

It is important to use the right methods for the right problem.  
Some methods may be very good on certain systems,  
But may not be overall competitive with other techniques.

TABLE XXIII. Relative performance of selected approaches for various few-body systems.

System	Hylleraas	CI	Hyperspherical	QMC	ECG methods
Atomic systems $N \leq 3$	Extreme precision	Good	Good	Good	High precision
Atomic systems $4 \leq N \leq 6$	Not used	Very good	Hardly used	Good	Excellent
Cluster systems	Fair	Poor	Good	Very good	Excellent
Small molecular systems	Only two-electron diatomic	Good	Hardly used	Good	Excellent
Scattering	Excellent for resonances	Very good	Excellent	Good for difficult systems	Good for difficult systems
Cold atoms	Hardly used	Hardly used	Excellent	Excellent	Excellent
Electronic quantum dots	Hardly used	Very good	Hardly used	Very good	Very good
Excitons and related systems	Hardly used	Hardly used	Hardly used	Very good	Excellent
Nuclear and subnuclear systems ( $N \leq 5$ )	Hardly used	Very good	Hardly used	Very good	Very good
All systems ( $N > 6$ )	Not used	Very good	Not used	Excellent	Rarely used

From Mitroy et al. RMP 2013

# An Example H<sub>2</sub>

Ground state energy of H<sub>2</sub> (QMC)

$$-1.164\,0239 \pm 0.000\,0009$$

- Quantum Monte Carlo can treat para-hydrogen exactly in its ground state. Chen and Anderson calculated one of the most highly accurate QMC solutions with a simple wave function.
- QMC is exact, but.....

$$\phi_T = \phi_1 \phi_2 \phi_3 \phi_4.$$

The four terms are

$$\phi_1 = \exp(-ar_{13}) + \exp(-ar_{14}),$$

$$\phi_2 = \exp(-ar_{23}) + \exp(-ar_{24}),$$

$$\phi_3 = \exp\left(\frac{br_{12}}{1 + br_{12}}\right),$$

$$\phi_4 = \exp[-d(r_{34} - c)^2],$$

Chen-Anderson JCP 1995

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Chen-Anderson JCP 1995

The best current ECG result

$$-1.164\,025\,030\,84(21)$$

# How is convergence determine?

The ECG method employs a basis set that is complete, and therefore can be extrapolated to the the complete basis set limit

First H<sub>2</sub> ECG Paper: Kinghorn and Adamowicz 1999

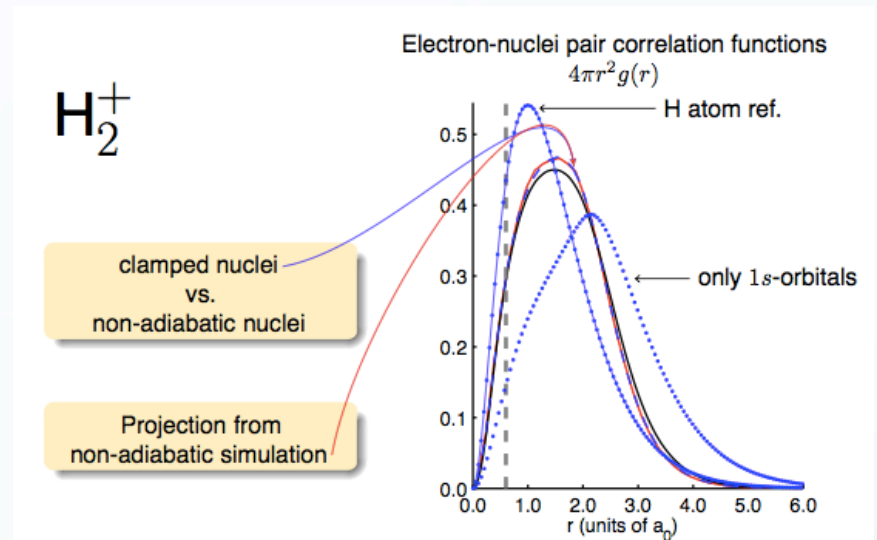
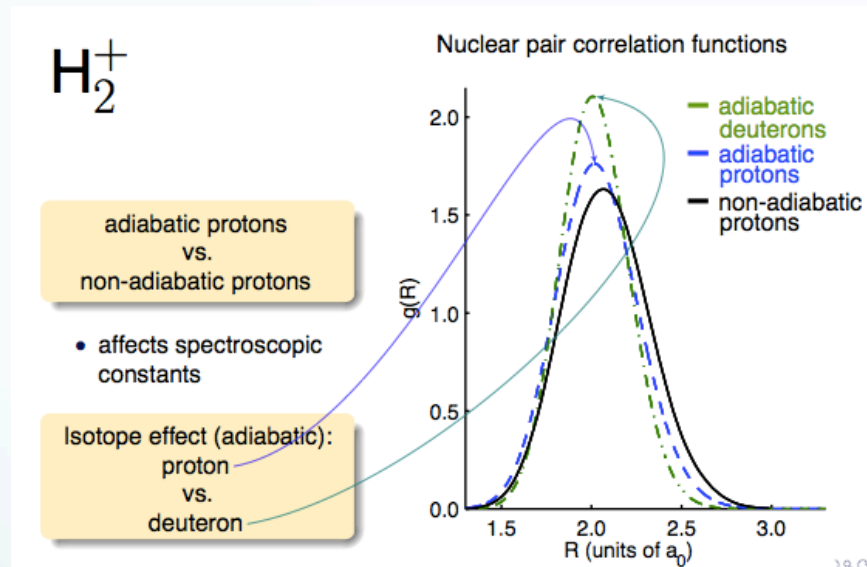
TABLE I. Energy expectation value for the dihydrogen nonadiabatic ground state using a 512 term correlated Gaussian wave function and comparison with literature values are shown. Energy is given in hartrees.

-1.164 025 023 2	This work (H mass = 1836.152 693 a.u.); variational, 512 basis functions
-1.164 025 018	Wolniewicz Ref. [8] (H mass = 1836.1527; high accuracy adiabatic and nonadiabatic corrections
-1.164 024 13	Bishop and Cheung Ref. [9] (H mass = 1836.15 a.u.); variational, 1070 basis functions
-1.164 023 9	Chen and Anderson Ref. [10] (H mass not given); quantum Monte Carlo

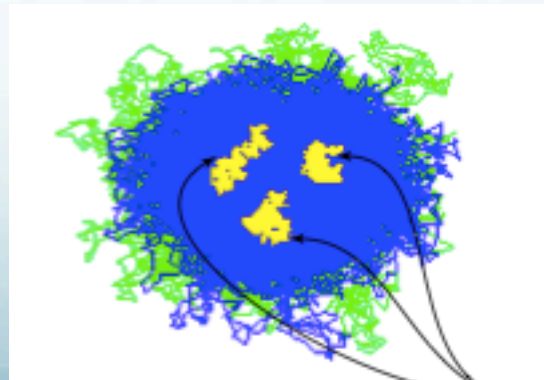
Latest H<sub>2</sub> ECG Paper: Bubin, S., et al. 2009

$v$	$M = 7000$	$M = 8000$	$M = 9000$
0	-1.16402503072	-1.16402503079	-1.16402503082
	$M = 10000$	$M = 10000^a$	Est. error
	-1.16402503084	-1.16402503084 ( $-2.1 \times 10^{-10}$ )	$6 \times 10^{-11}$

# What about finite temperatures



Kylanpaa Thesis 2011



# Finite temperatures?

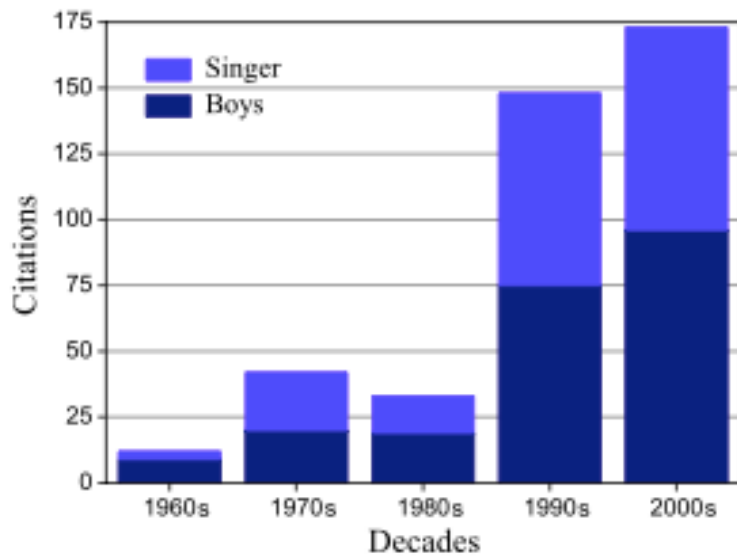
It is possible to simulate many excited states also with the ECG method.

$v$	$M = 7000$	$M = 8000$	$M = 9000$	$M = 10000$	$M = 10000^a$
0	-1.16402503072	-1.16402503079	-1.16402503082	-1.16402503084	-1.16402503084 ( $-2.1 \times 10^{-10}$ )
1	-1.14506537180	-1.14506537193	-1.14506537202	-1.14506537209	-1.14506537210 ( $-5.6 \times 10^{-10}$ )
2	-1.12717793514	-1.12717793540	-1.12717793558	-1.12717793572	-1.12717793573 ( $-1.3 \times 10^{-9}$ )
3	-1.11034047802	-1.11034047842	-1.11034047872	-1.11034047893	-1.11034047896 ( $-1.7 \times 10^{-9}$ )
4	-1.09453917164	-1.09453917213	-1.09453917248	-1.09453917277	-1.09453917280 ( $-2.2 \times 10^{-9}$ )
5	-1.07976944479	-1.07976944555	-1.07976944606	-1.07976944642	-1.07976944647 ( $-3.5 \times 10^{-9}$ )
6	-1.06603723345	-1.06603723427	-1.06603723496	-1.06603723543	-1.06603723550 ( $-3.9 \times 10^{-9}$ )
7	-1.05336075872	-1.05336075984	-1.05336076064	-1.05336076124	-1.05336076136 ( $-5.2 \times 10^{-9}$ )
8	-1.04177303330	-1.04177303480	-1.04177303576	-1.04177303648	-1.04177303663 ( $-6.7 \times 10^{-9}$ )
9	-1.03132537776	-1.03132537950	-1.03132538074	-1.03132538164	-1.03132538188 ( $-8.6 \times 10^{-9}$ )
10	-1.02209238958	-1.02209239171	-1.02209239319	-1.02209239417	-1.02209239440 ( $-1.0 \times 10^{-8}$ )
11	-1.01417905483	-1.01417905732	-1.01417905898	-1.01417906013	-1.01417906044 ( $-1.2 \times 10^{-8}$ )
12	-1.00773110799	-1.00773111095	-1.00773111280	-1.00773111411	-1.00773111446 ( $-1.4 \times 10^{-8}$ )
13	-1.00295039306	-1.00295039616	-1.00295039813	-1.00295039947	-1.00295039985 ( $-1.4 \times 10^{-8}$ )
14	-1.00011594097	-1.00011594357	-1.00011594522	-1.00011594635	-1.00011594657 ( $-1.2 \times 10^{-8}$ )

Bubin, S., et al. 2009



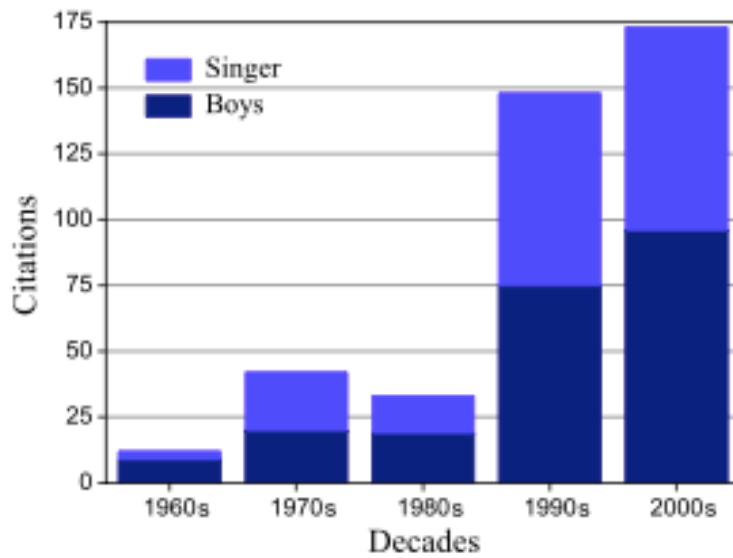
# High accuracy simulations



From Mitroy et al. RMP 2013



# High accuracy simulations



From Mitroy et al. RMP 2013

## Further Computations of the He Atom Ground State

Charles Schwartz \*

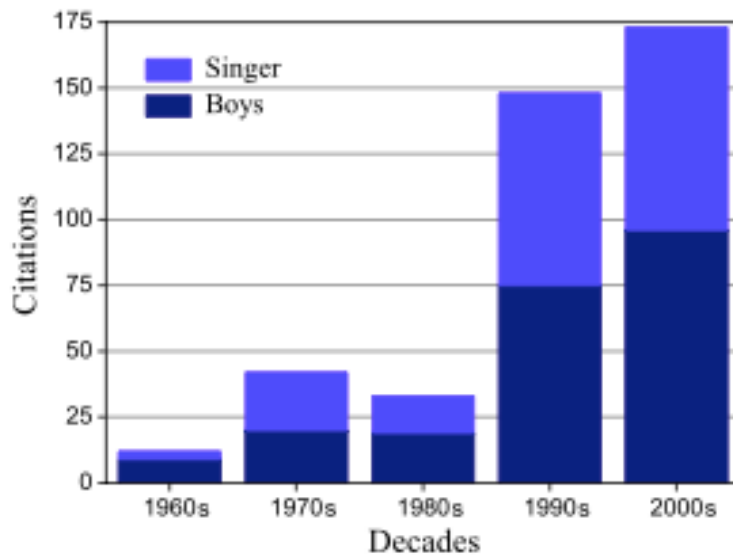
*Department of Physics, University of California  
Berkeley, California 94720*

### Abstract

Recently reported computations have been extended to give ten more decimals of accuracy in the ground state energy of the Schrodinger equation for the idealized Helium atom. With the F basis - Hylleraas coordinates with negative powers and a logarithm of  $s$  - carried to the fiftieth order ( $N = 24,099$  terms) we find the eigenvalue

$$E = -2.90372\ 43770\ 34119\ 59831\ 11592\ 45194\ 40444\ 66969\ 25309 \dots$$

# High accuracy simulations



From Mitroy et al. RMP 2013

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$$E^* = -2.90372\ 43770\ 34119\ 59831\ 11592\ 45194\ 40444\ 66969\ 25310\ 5$$

# Fixed-ion Systems

## ECG/HYL

He atom

---

CI (Bromley and Mitroy, 2007a)	8 586	−2.903 712 786
ECG (Rybak, Szalewicz, and Jeziorski, 1989)	100	−2.903 723 818 0
ECG (Cencek and Kutzelnigg, 1996)	1 200	−2.903 724 377 030 1
ECG (Komasa, 2001)	600	−2.903 724 377 022
HYL (Drake, Cassar, and Nistor, 2002)	2 358	−2.903 724 377 034 119 598 305
HYL (Korobov, 2002)	5 200	−2.903 724 377 034 119 598 311 1587
ICI (Nakashima and Nakatsuji, 2007)		−2.903 724 377 034 119 598 311 159 245 194 404 446 696 905 37
HYL-LOG (Schwartz, 2006a, 2006b)	24 099	−2.903 724 377 034 119 598 311 159 245 194 404 446 696 925 309 838

From Mitroy et al. RMP 2013

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From Mitroy et al. RMP 2013

# Fixed-Ion Systems

## ECG/HYL/CI

Li( $1s^2 2s$ )	CI (Jitrik and Bunge, 1997)		-7.478 025 4
	ECG (Komasa, 2001)	1 536	-7.478 060 314 3
	ECG (Stanke <i>et al.</i> , 2008b)	10 000	-7.478 060 323 81
	HYL (L. M. Wang <i>et al.</i> , 2011)	26 520	-7.478 060 323 910 134 843
Li( $1s^2 2p$ )	ECG (Komasa, 2001)	3 700	-7.410 156 22
	HYL (L. M. Wang <i>et al.</i> , 2011)	30 224	-7.410 156 532 650 66
Li( $1s^2 3d$ )	ECG (Sharkey, Bubin, and Adamowicz, 2011c)	4 000	-7.335 523 542 97(60)
	HYL (Wang <i>et al.</i> , 2012)	32 760	-7.335 523 543 524 685
Be <sup>+</sup> ( $1s^2 2s$ )	ECG (Stanke <i>et al.</i> , 2008a)	8 000	-14.324 763 176 4
	HYL (Puchalski, Kędziera, and Pachucki, 2009)	13 944	-14.324 763 176 790 150
Li <sup>-</sup> ( $1s^2 2s^2$ )	ECG (Bubin, Komasa <i>et al.</i> , 2009)	10 000	-7.500 776 613 4(200)
Be( $1s^2 2s^2$ )	CI (Bunge, 2010)	2 614 689	-14.667 347 30
	ECG (Komasa, Cencek, and Rychlewski, 1995)	1 200	-14.667 355 0
	ECG SVM (Mitroy, 2011)	1 800	-14.667 354 0
	ECG (Komasa, Rychlewski, and Jankowski, 2002)	1 600	-14.667 355 5
	ECG (Stanke, Komasa <i>et al.</i> , 2009)	10 000	-14.667 356 486(15)
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# Fixed-Ion Systems

## ECG/CI/DMC

Be( $1s^2 2s 2p$ )	ECG (Bubin and Adamowicz, 2009)	5 000	−14.473 451 311(70)
Be( $1s^2 2s 3s$ )	ECG (Stanke, Komasa <i>et al.</i> , 2009)	10 000	−14.418 240 328(30)
B <sup>+</sup> ( $1s^2 2s^2$ )	CI (Almora-Diaz and Bunge, 2010)	530 335	−24.348 861 07
	ECG (Komasa, Rychlewski, and Jankowski, 2002)	1 600	−24.348 883 2
	ECG (Bubin <i>et al.</i> , 2010b)	10 000	−24.348 884 446(35)
C <sup>2+</sup> ( $1s^2 2s^2$ )	ECG (Komasa, Rychlewski, and Jankowski, 2002)	1 600	−36.534 849 7
	ECG (Bubin <i>et al.</i> , 2010a)	10 000	−36.534 852 338(35)
B( $1s^2 2s^2 2p$ )	CI (Almora-Diaz and Bunge, 2010)	16 352 813	−24.653 837 33
	ECG (Bubin and Adamowicz, 2011b)	5 100	−24.653 866 08(250)
	DMC (Seth, Ríos, and Needs, 2011)		−24.653 79(3)
B( $1s^2 2s^2 3s$ )	ECG (Bubin and Adamowicz, 2011b)	5 100	−24.471 393 06(50)
C <sup>+</sup> ( $1s^2 2s^2 2p$ )	ECG (Bubin and Adamowicz, 2011a)	5 100	−37.430 880 49(250)
	DMC (Seth, Ríos, and Needs, 2011)		−37.430 73(4)

From Seth et al.  
2011

	Li ( <sup>2</sup> S)	Be ( <sup>1</sup> S)	B ( <sup>2</sup> P)	C ( <sup>3</sup> P)	N ( <sup>4</sup> S)
VMC	−7.478034(8)	−14.66719(1)	−24.65337(4)	−37.84377(7)	−54.5873(1)
DMC	−7.478067(5)	−14.667306(7)	−24.65379(3)	−37.84446(6)	−54.58867(8)
$E_{\text{HF}}$	−7.432727	−14.573023	−24.529061	−37.688619	−54.400934
$E_{\text{ref}}$	−7.47806032	−14.66736	−24.65391	−37.8450	−54.5892
$E_{\text{HF}} - E_{\text{ref}}$	0.0453333	0.094337	0.124849	0.156381	0.188266
VMC-corr%	99.94(2)%	99.82(1)%	99.57(3)%	99.21(4)%	98.99(5)%
DMC-corr%	100.01(1)%	99.943(7)%	99.90(2)%	99.65(4)%	99.72(4)%

# ECG Non-adiabatic GS energies

Accuracy drops orders of magnitudes as systems get larger, for specialized basis set calculations

TABLE XIII. Total nonadiabatic ground state energies (in hartree) of selected small diatomic molecules. In parentheses we show the estimated difference between the variational upper bound and the exact nonrelativistic energy.

System	Basis size	Energy	Reference
H <sub>2</sub>	10 000	−1.164 025 030 84(21)	Bubin, Leonarski <i>et al.</i> (2009)
HD	10 000	−1.165 471 922 0(20)	Bubin, Stanke, and Adamowicz (2011b)
HeH <sup>+</sup>	8 000	−2.971 078 465 9(5)	Stanke <i>et al.</i> (2008a)
LiH	7 200	−8.066 437 1(15)	Bubin, Adamowicz, and Molski (2005)
LiH <sup>−</sup>	3 600	−8.067 382 5(50)	Bubin and Adamowicz (2004)
BeH	4 000	−15.242 03(10)	Bubin and Adamowicz (2007)
BH	2 000	−25.280 3(10)	Bubin, Stanke, and Adamowicz (2009)

From Mitroy et al. RMP 2013

# What has been done with full electron-ion QMC

PHYSICAL REVIEW B

VOLUME 36, NUMBER 4

1 AUGUST 1987

## Ground state of solid hydrogen at high pressures

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(Received 13 March 1987)

VOLUME 70, NUMBER 13

PHYSICAL REVIEW LETTERS

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## Crystal Structure of Atomic Hydrogen

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(Received 14 August 1992)

## Improved quantum Monte Carlo calculation of the ground-state energy of the hydrogen molecule

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(Received 30 August 1994; accepted 8 November 1994)

# What has been done with full electron-ion QMC

PHYSICAL REVIEW B

VOLUME 36, NUMBER 4

1 AUGUST 1987

## Ground state of solid hydrogen at high pressures

$$\Psi(\{\mathbf{r}\}, \{\mathbf{R}\}) = \exp \left[ - \sum_{i \neq j} u_{ee}(\mathbf{r}_i - \mathbf{r}_j) - \sum_{iJ} u_{ep}(\mathbf{r}_i - \mathbf{R}_J) \right] D^\dagger \{ \phi_k(\mathbf{r}_l) \} D^\dagger \{ \phi_k(\mathbf{r}_l) \},$$

In the case of the dynamic lattice, there are additional protonic terms in the trial wave function Eq. (1), namely, a **proton-proton correlation function  $u_{pp}$** , also derived within the RPA [15], and a **product of Gaussian orbitals** centered on lattice sites. The size of these Gaussian or-

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$$\phi_T = \phi_1 \phi_2 \phi_3 \phi_4.$$

The four terms are

$$\phi_1 = \exp(-ar_{13}) + \exp(-ar_{14}),$$

$$\phi_2 = \exp(-ar_{23}) + \exp(-ar_{24}),$$

$$\phi_3 = \exp\left(\frac{br_{12}}{1+br_{12}}\right),$$

$$\phi_4 = \exp[-d(r_{34}-c)^2],$$

ground-state energy

# QMC electron/ion wave functions

We consider three forms of electron-ion wave functions

- Ion independent determinants
- Ion dependence introduced through the basis set
- Full ion dependence

$$\Psi(r, R) = e^{J(r, R)} \phi(R) \sum_i \alpha_i^* D_i(r)$$

$$\Psi(r, R) = e^{J(r, R)} \phi(R) \sum_i \alpha_i^* D_i(r, R^*)$$

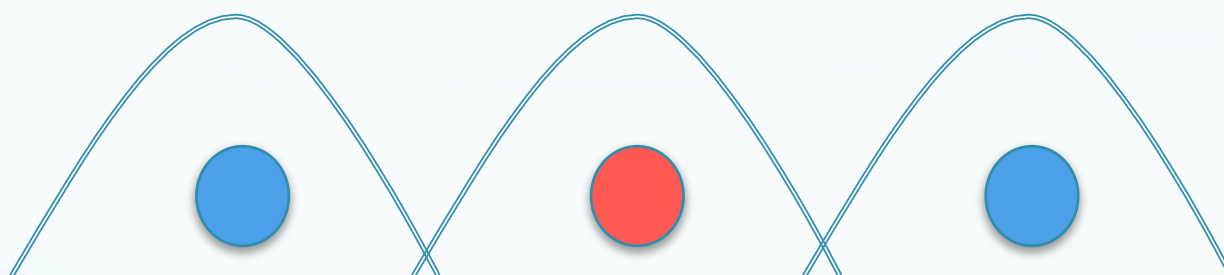
$$\Psi(r, R) = e^{J(r, R)} \phi(R) \sum_i \alpha_i D_i(r, R),$$

$$\phi(R) \propto \prod_i e^{-a_{ij}(|R_i - R_j| - b_{ij})^2}$$

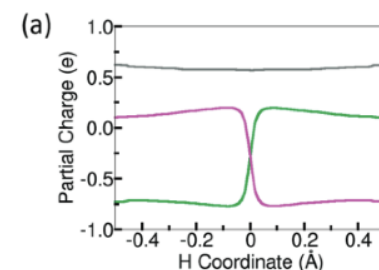
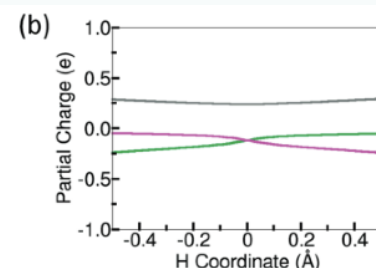
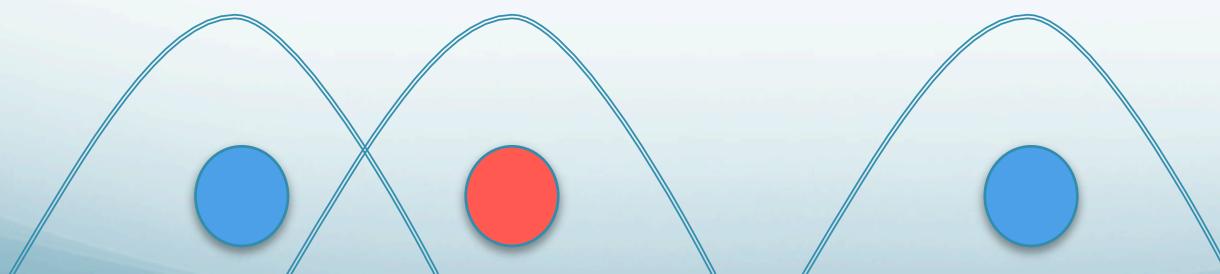
$$\theta(r) = \sum_{ji} \gamma_j(r - \bar{R}_i),$$

# Benefits of using local orbitals

-A simple way to perform non adiabatic calculations is to make use Of the localized basis set and drag the orbitals when the ions move



Move the Ion and Drag the Orbital





# FN-DMC $H_2$

- Three different forms of the wave function considered
- The “nr” wave functions are currently in the release version of QMCPACK. FN-DMC fixes a lot of deficiencies in this form of the wave function
- What are the limits of accuracy for FN-DMC?

	HF	CI-nr	CI
VMC-fixed	-1.1360(1)		-1.1742(1)
variance-fixed	0.147		0.016
VMC-full	-1.1197(1)	-0.751(1)	-1.1617(1)
variance-full	0.15	0.864	0.021
DMC-full	-1.1639(2)	-1.163(1)	-1.16401(5)
variance-full	0.122	0.111	0.021
Comparisons	Our Work	ECG	
	-1.16401(5)	-1.16402503084 [1, 28]	



# FN-DMC LiH

- FN-DMC and ECG are well above experimental energy. But ECG is converged to very high accuracy.
- Symmetrizing the wave function is incredibly important for VMC. Not as important for DMC.
- Larger molecules also calculated such as H<sub>2</sub>O and FHF<sup>-</sup>.

	HF	CASSCF-nr	CASSCF
VMC-fixed	-8.06434		-8.0691(2)
variance-fixed	0.035		0.013
DMC-fixed			-8.07045(2)
VMC-full	-8.0596(1)	-8.0<	-8.0648(2)
variance-full	0.036	0.5>	0.015
DMC-full	-8.0655(2)	-8.0646(3)	-8.06628(2)
variance-full	0.036	0.022	0.015
Comparisons	Our Work	ECG	Experiment
	-8.06628(2)	-8.0664371 [29]	-8.0674 [2, 30]

# Improving wave functions

It is important to capture large changes in the electronic wave functions as the ions move

$$\Psi(r, R) = e^{J(r, R)} \phi(R) \sum_i \alpha_i^* D_i(r)$$

$$\Psi(r, R) = e^{J(r, R)} \phi(R) \sum_i \alpha_i^* D_i(r, R^*)$$

$$\Psi(r, R) = e^{J(r, R)} \phi(R) \sum_i \alpha_i D_i(r, R),$$

## Other Wave function to explore:

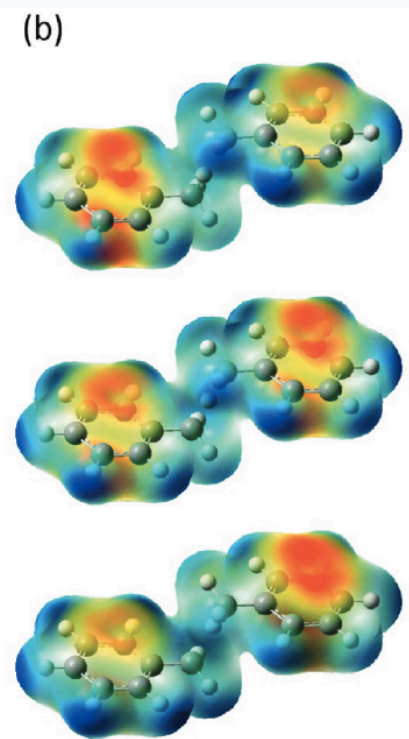
- Grid Based Wave functions
- Wannier functions and FLAPW
- Multi-determinant electron-ion wfs

## The exact molecular wavefunction as a product of an electronic and a nuclear wavefunction

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From Sirjoosingh et. al. JPCA

# Conclusions

- FN-QMC might be one of the only methods right now that can tackle non-adiabatic systems of more than 6 quantum particles with high accuracy
- For small systems it is possible to make use of quantum chemistry techniques to calculate highly accurate non-adiabatic wave functions
- There are many possibilities for improving wave function quality and running large systems with FN-QMC

The background of the slide is an abstract composition. The upper half is a pale, light blue sky with soft, wispy white clouds. The lower half features a series of horizontal, wavy bands in various shades of blue, creating a sense of depth and movement, reminiscent of a horizon or a stylized landscape.

# The End